FLOW-VACUUM PYROLYSIS OF BENZOBARRELENE ON ZEOLITES CATALYSTS. VI[1]

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Piroliza benzobiciclo[2.2.2]octatrienei (benzobarilena) a fost studiată în vid avansat şi atmosferă inertă, pe zeoliţi, între 200°C şi 300°C. Produşii de reacţie au fost identificaţi folosind gaz cromatografia cuplată cu spectrometria de masă. Este prezentată o comparaţie a pirolizei aceluiaşi compus pe zeoliţi şi pe cuarţ.

The pyrolysis of benzobiciclo[2.2.2.]octatriene (benzobarrelene) in flow-vacuum conditions (advanced vacuum, inert atmosphere) on zeolites between 200°C and 300°C is presented. The reaction products were identified by gas chromatography couplet with mass spectroscop. A comparison with the pyrolysis of the same compound performed on zeolites and on quartz is presented.

Keywords: benzobarrelene, flow-vacuum pyrolysis, zeolites

1. Introduction

The flow-vacuum pyrolysis (FVP) reactions of some dibenzocyclo-annelated systems (some alcohols and their corresponding acetates: **1** – **4**), in the presence of different acidic zeolites, in advanced vacuum and inert atmosphere were performed for the first time some years ago by Banciu and co-workers [1]:

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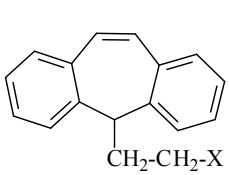
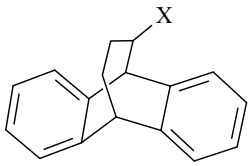
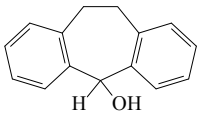


1, 2 (X = - OH; - $OCOCH_3$) **3, 4**



The thermal behavior of some other systems (**5 – 8**), in the flow-vacuum conditions on zeolites as catalysts, was also studied in our group [2]:



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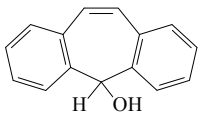

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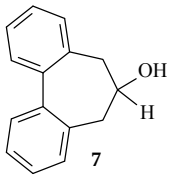

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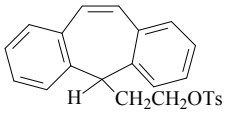

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The study of the thermal behavior of the benzobarrelene **9** in FVP on acid zeolites conditions performed for better understanding of the rearrangement mechanism during pyrolysis.

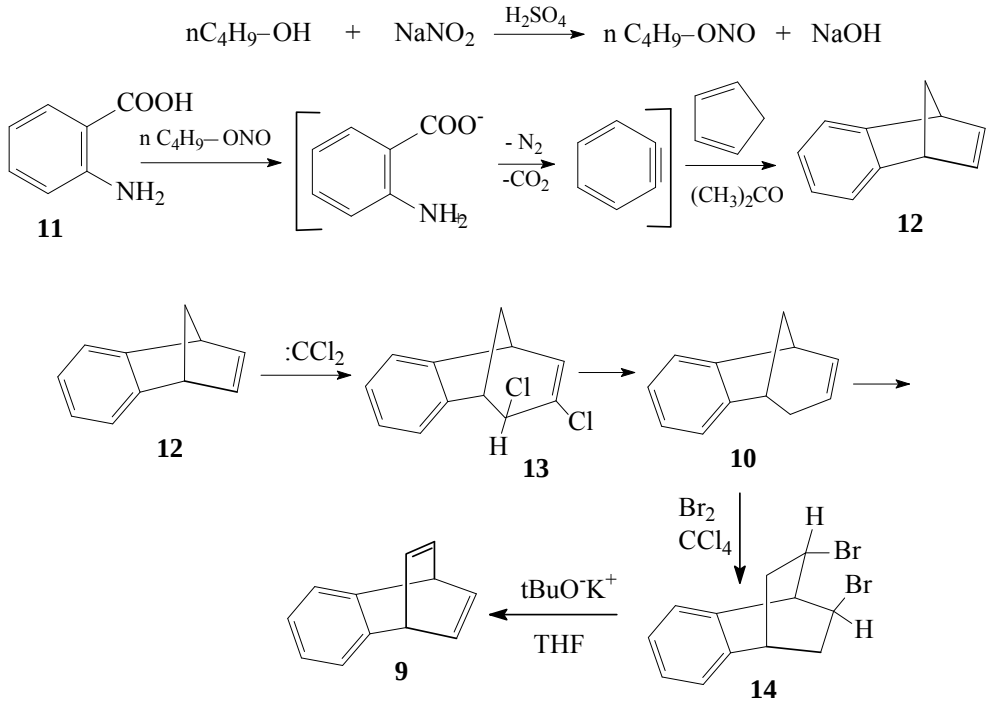
In this paper we present the results obtained for the flow-vacuum pyrolyses (FVP) of the benzobarrelene on HZSM-5 and on Montmorillonite K10 as catalysts, between 200°C and 300°C, at 0,2 Torr, in inert atmosphere.

2. Experimental

The synthesis of benzobarrelene was performed using according to Scheme 1 [3] starting from o-aminobenzoic acid (**11)**, as described in scheme 1.

The obtained benzobarrelene **9** had m.p. $64^0 – 66^0$C (lit.[4] $64.5^0 – 66.5^0$C) and the spectral data described in literature [4].

The pyrolyses of benzobarrelene **9** were performed in an original apparatus [4], in flow-vacuum conditions (advanced vacuum – 0.2 Torr; argon inert atmosphere with flow rate of 4 mL/min.), in a vertical glass tube (10 mm diameter, 60 cm length), using zeolites as catalyst. The filled zeolite zone (10 cm length) was heated using an electrical cylindrical vertical oven in a temperature range between 200° and 300°C. The temperature was continuously measured by a thermocouple and the pressure was checked with a vaccum gauge. At the cold lower end of the pyrolysis tube, the final reaction mixture was accumulated as uncolored viscous liquid.



Scheme 1

The reaction mixture was further dissolved in dichloromethane, the solvent was evaporated in vacuo (600 torr) and the solid residue was analysed by gas chromatography coupled with mass spectrum (Agilent 6890 GC coupled with 5975N MS; injection 1 μL at 280^0C; oven: 70-280^0C/7 deg/min; transfer line 230^0C; mass range 46-550; ionization EI 70 eV).

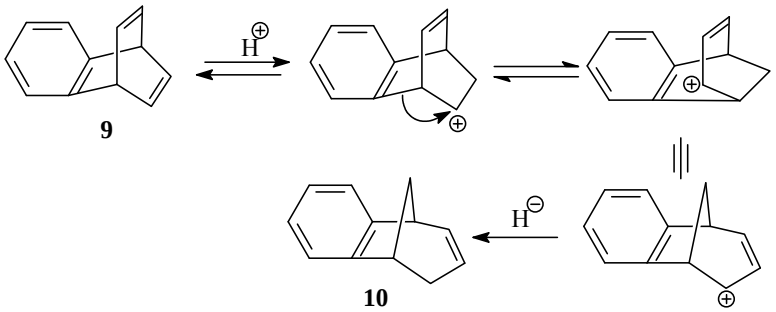
3. Results and discussion

The thermal behaviour of the benzobarrelene in FVP conditions on zeolites (HZSM-5 and Montmorillonite K10) was studied. The surface acidic properties of the catalyst HZSM 5 were determined through chemosorption of ammonia followed by programmed thermodesorption in a flow-system.

The main characteristics of this catalyst are presented as follows:

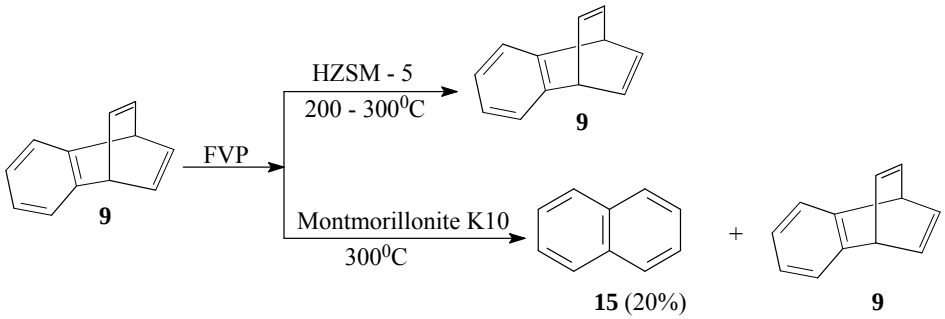
- SiO_2/ Al_2O_3 Molar ratio = 20
- Si/Al Atomic ratio = 40
- Langmuir specific surface = 485 $m^2 g^{-1}$
- Volum of pores = 0.16 $cm^3 g^{-1}$

If, as we assumed earlier [1b-c], the acidic properties of the zeolite induce the observed ionic rearrangements of the substrate, in the case of the benzobicyclo[2.2.2]octatriene, benzobarrelene **9**, this would imply the transfer of a proton to the substrate, with, probably, the final formation of the benzobicyclo[3.2.1]octadiene (**10**) (Scheme 2):



Scheme 2

Unfortunately, the pyrolyses mixtures obtained on acid zeolite HZSM-5 showed only untransformed benzobarrelene. This means that this compound is stable in these FVP conditons, between 200^0C and 300^0C.

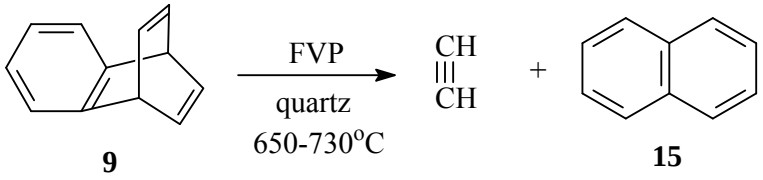


Scheme 3

In the same FVP condition, at 300^oC, but using as zeolite catalyst the Montmorillonite K10, was obtained as single pyrolysis product the naphthalene **15** (20%) (Scheme 3):

The formation of naphthalene in Montmorillonite K10 catalysis could be explained by the catalyst capacity to form a complex with acetylene which facilitates the [4+2] retrocyclization.

The pyrolysis of benzobarrelene in flow vacuum system (nitrogen atmosphere, quartz tube, between 650^0C – 730^0C) in benzene solution, afforded 100% naphthalene [5] by radical mechanism (Scheme 4):



Scheme 4

The thermal stability of benzobarrelene in static conditions was also studied, when the naphthalene formation was observed also [6].

In this work was studied the thermal behavior of benzobarrelene in dynamic conditions (FVP). We can affirm that on acid zeolite HZSM-5 between 200°C and 300°C the pyrolyses of benzobarrelene did not occur. It is possible that this catalyst has not the capacity to form a complex with acetylene (the second gaseous pyrolysis product) and also it was not observed an expected skeleton rearrangement with formation of benzobiciclo[3.2.1]octadiene (**10)** (Scheme 2).

Using as catalyst Montmorillonite K10 at 300°C, benzobarrelene was partially transformed and the pyrolysis product was naphthalene. The formation of naphthalene in Montmorillonite K10 catalysis may be explained by the capacity of this catalyst to form a complex with acetylene and thus to facilitate the [4+2] retrocyclization. The used catalysts cannot transfer a proton to the substrate.

4. Conclusions

In this work, the studies were focused on:

- the thermal behaviour of benzobarrelene in flow vacuum pyrolysis in inert atmosphere on zeolites;
- the comparison of thermal decomposition of benzobarrelene in FVP conditions on zeolites catalyst *versus* quartz;
- the naphthalene was the main pyrolysis product only using the Montmorillonite K10 as catalyst.

Acknowledgements

The National University Research Council, from the Roumanian Ministry of Education, Research and Youth is gratefully acknowledged for the financial support of the research through the exploratory, "A New Synthetic and Mechanistic Approach of Flow Vacuum Pyrolysis Reactions", Grant 1557/ 2009.

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